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Chapter 5

**FLAME RETARDANT MECHANISMS:
RECENT DEVELOPMENTS**

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SUMMARY

The principal mechanisms by which flame retardance is conferred on polymeric substrates are reviewed in the light of the most recent experimental work. The six elements which are the active constituents of the most widely used flame-retardant systems are chlorine and bromine (Group VII), phosphorus and antimony (Group V) and boron and aluminium (Group III).

Flame retardance involves the interference with one or more of the various stages involved in the complex process of polymer combustion. This action may be purely physical in nature, although it is most likely to be effective if the rate and course of some of the constituent chemical reactions are also altered.

Gas-phase mechanisms may involve the destruction of those species which propagate the flame reactions or simply the absorption of heat with an accompanying reduction in gas temperature.

Condensed-phase mechanisms usually involve changes in the rates of pyrolytic or thermo-oxidative breakdown of the polymeric structure.

1. INTRODUCTION

Natural organic polymers, principally cellulose, have been an important part of man's environment for many centuries. They have complex

structures which in general withstand well prolonged exposure to the atmosphere. Synthetic polymers are relatively new materials which have been in commercial production for only about 50 years. They are relatively simple materials composed of few different monomeric units and they have been designed for applications where some combination of mechanical properties, and perhaps colour, is vital to their effectiveness. They are however in general more susceptible to oxidative attack than natural polymers.

The prevention of the loss of the attractive properties of polymers during use is usually termed stabilisation. The processes responsible for deterioration may consist of photo-oxidative, thermo-oxidative, hydrolytic, solvolytic or other chemical degradation reactions resulting from normal exposure. They do not, in general, involve an extensive breakdown of the polymeric structure; the materials lose their effectiveness long before they have broken down completely. The additives (stabilisers) normally used for this purpose must inhibit processes which are slow but which should not be allowed to occur to any significant extent.

Although only synthetic polymers normally need stabilisation, both natural and synthetic polymeric materials are inherently flammable. The inhibition of polymer combustion involves substrates which are to be employed either under conditions where they may be exposed to local high temperatures or in applications where their breakdown may produce undesirable hazards. The conferment of flame retardance is the process by which polymers are either protected from undergoing a rather more complete destruction of the material than simple loss of mechanical properties or are forced to change the course of this decomposition so as to form products which are less hazardous.

It is not surprising that interest in treatments to reduce the flammability of organic polymers, which are entirely different from those used for their stabilisation, can be traced back to ancient times. The empirical application of additives started with the use of compounds of aluminium, which is still a constituent of one of the most widely used flame retardants. Solutions of alum (potassium aluminium sulphate) are known to have been used by the Egyptians to inhibit the combustion of wood, while nowadays many synthetic thermoplastics are treated with aluminium oxide trihydrate.¹

Gay-Lussac carried out in France one of the first detailed systematic studies of the flame retardance of cellulosic textiles² and Perkin continued this work in England towards the end of the nineteenth century, although many of his results were not published until after his death.³⁻⁶ These researches were, of necessity, largely empirical and it is only in the last 20

years or so that attempts have been made to elucidate the fundamental mechanisms of flame retardance. Some reviews have dealt with several aspects of this subject⁷⁻¹² and the next chapter deals with one aspect in some depth. The remainder of this chapter will present some recent developments.

2. COMBUSTION OF POLYMERS

The burning of a polymer is a complex process which involves several interrelated and interdependent stages. To understand the mechanism of flame retardance it is essential to outline these stages, even if superficially. The heat supplied to the polymer is responsible for bringing about its thermal decomposition. This can occur by several different mechanisms: scission of the main polymer chain, i.e. polymeric backbone, scission of the bonds linking the polymer chain to substituents, or cyclisation processes. If polymer chain scission takes place at the terminal unit, i.e. end-chain-scission, the result is depolymerisation to yield identical monomer-type molecules. The other modes of decomposition yield different small molecules or fragments which are liberated into the gas phase. These volatile products may subsequently ignite in admixture with the surrounding gaseous oxidant. This combustion liberates more heat which is then fed back to the solid phase of the polymer causing its further breakdown. This model of burning polymer will be discussed in more detail in Chapter 6.

Smouldering combustion occurs as an ignition of the solid char formed as a consequence of the initial thermal or thermo-oxidative decomposition, at temperatures which are frequently lower than those required for the ignition of the gaseous products. Glowing combustion is distinguished from smouldering combustion in that it is usually accompanied by a pale blue flame characteristic of the conversion of CO to CO₂.

In principle it is possible to affect each one of the separate stages individually. In practice, however, the technology of flame retardance usually involves either the use of additives or the replacement of monomers by less flammable analogues. These compounds do not very often confine their action to one of the separate stages involved in polymer combustion. Many, if not most, flame retardants may function simultaneously by several different mechanisms, often depending on the nature of the organic polymer. It is, therefore, more systematic to deal with individual classes of additives, according to the principal element they include, and explain their

mechanisms of action, rather than to discuss in depth the different mechanisms by which a flame retardant may operate. Before this is attempted, however, some of the possible mechanisms of flame retardant action will be outlined.

3. FLAME RETARDANCE

Two distinct types of flame retardant must be recognised.

Reactive flame retardants are compounds usually containing a heteroelement which can be used to substitute one or more of the normal comonomers. This substituent then becomes an integral part of the repeating structural unit of the polymer. Reactive flame retardants can also be chemically incorporated, in smaller proportions, usually during the polymerisation process, so that only partial replacement is effected and only occasional structural units are altered.

Additive flame retardants are incorporated into polymers by being physically mixed with the polymer, normally after the polymerisation is complete. They may be more or less uniformly distributed in the bulk of the condensed polymer phase or coated on its surface but they do not affect the chemical structure of any of the monomeric units.

When the combined effect of two or more flame retardants is larger than the sum of the effects of each of the individual compounds, synergism is said to occur. Antagonism results when the combined effect of two or more flame retardants is smaller than the sum of their individual effects. Synergistic or antagonistic flame retardance can also occur as a result of the interaction of an additive with a heteroelement already present in the polymer structure.

The ideal flame-retardant polymer is one which is completely thermally stable and which does not break down at all. Although many polymers have been developed which have considerable thermal stability¹³⁻¹⁸ they all eventually burn if they are basically organic in nature.¹⁹ The great advantage that these materials offer is, of course, that they are very unlikely to be the material first ignited. If their decomposition products can form a flammable mixture, however, they will then eventually fuel the flames of an already existing fire. These polymers are generally very expensive to produce and do not normally possess the engineering properties which make the present high-tonnage polymers so attractive. It is therefore probable that the production of thermally stable polymers will in future remain a process of rather more academic than industrial interest, except for specific applications.

The most obvious effect of an additive is to retard the thermal decomposition of the polymer. This is, of course, similar in its effects to the preparation of an intrinsically thermally stable polymer. It is also possible, and sometimes desirable, to affect the breakdown of a polymer by increasing its rate of decomposition and thus forming a non-ignitable mixture, either because the latter is too fuel-rich or because the products formed are now intrinsically non-flammable.

The use of 'fillers' represents another flame-retardant mechanism. The inert compounds generally used are introduced into the polymer and may act as heat sinks, so that the temperature never reaches levels high enough for the polymer to suffer significant breakdown.

Another possible mechanism of action is the creation of a non-flammable protective layer which then insulates the polymer from the source of heat or excludes the gaseous oxidant from the polymer surface. If such a coating is formed only by the decomposition of the additive at high temperatures and if the char resulting from these condensed-phase reactions can trap the evolved gases and use them to cause expansion into a carbonaceous foam, then an intumescent coating results. Direct external application of a non-flammable protective surface layer results in a non-intumescent coating.

All the treatments mentioned affect mainly the thermal decomposition of the polymer. The inhibition of the flame reactions can be brought about either by chemical or by physical means. Chemical action usually involves the replacement of reactive species by less reactive ones (see Chapter 6). A physical mechanism could be the production of small non-gaseous particles (i.e. mists) which can increase the rate of chain-termination by acting as 'third bodies' or 'walls' for the destruction of radicals or may even 'smother' the flames by excluding the gaseous oxidant. Another physical mechanism involves the release from the additive of inert gases which may produce a mixture too fuel-lean to be flammable.

It should, at least in principle, be possible to inhibit the transfer of heat back from the flame to the solid polymer phase. This can be achieved in practice as a result of the endothermic decomposition of the additives or the promotion of melting and dripping following depolymerisation or by the process known as ablation where entire burning sections of the polymer 'drop off'. In all these cases a large proportion of the heat of combustion is removed from the critical zone.

The inhibition of smouldering or glowing combustion is slightly more complex than that of flaming combustion because it is more difficult to envisage well-defined separate stages. The alteration of the initial

breakdown process is analogous to the action in the case of flaming combustion, i.e. the mechanism may involve chemical inhibition, fillers or coatings. On the other hand, the burning of the char is usually inhibited by specific additives which have very little effect on luminous flames and vice versa.

The information that is most frequently sought about the mechanisms of action of specific flame retardants relates to whether they act primarily in the gas phase or in the condensed phase. It is still a matter of some controversy whether oxidative surface reactions are important in the combustion process. For some polymers (e.g. polypropylene) oxygen in the surrounding atmosphere is claimed to be involved in the initial breakdown.^{20,21} For other polymers (e.g. polystyrene) radiant pyrolysis studies have shown that it makes no difference whether or not the surrounding atmosphere contains oxygen.²²

It is widely believed that, when the action of the flame-retardant additive is affected by the structure of the polymer substrate but not by the nature of the gaseous oxidant, then the mechanism is likely to involve an alteration in the condensed-phase decomposition of the polymer. If, however, the flame-retardant action changes when the oxidising atmosphere is varied, then, although it would be expected that the additive acts in the gas phase, it may only be influencing surface oxidative reactions while acting from the condensed phase. The mechanism of action may be assumed to be predominantly gas-phase if additionally the nature of the polymer does not influence the effect of the flame retardant.

The action of those additives used for the retardation of smouldering can occur both in the gas phase (i.e. halogens or sulphur dioxide^{23,24}) and in the condensed phase (i.e. borates or phosphates²⁵).

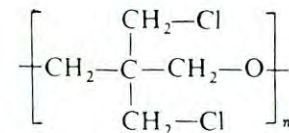
One of the tools most frequently used for elucidating flame retardant mechanisms is the determination of the limiting oxygen index (LOI), which corresponds to the minimum percentage of oxygen needed in an otherwise inert atmosphere to sustain the combustion of a polymer.²⁶ This is the basis of standard tests (ASTM D2863, BS 2782-141, ISO draft version) but is also of great value for fundamental research on account of the variety of parameters which can be altered. Typically oxygen is replaced as the oxidising gas by nitrous oxide to investigate whether there is a gas-phase mechanism of action of flame retardants.

In the following sections the effects of the most important elements with a flame-retardant action will be discussed. These are boron and aluminium (Group III), phosphorus and antimony (Group V) and chlorine and bromine (Group VII). Other elements have also been found to confer flame

retardance but they are either much less widely used or have less well-defined effects. Among these other elements mention will be made of nitrogen, molybdenum, zirconium, titanium, tin and sulphur.

4. CHLORINE

The fact that chlorine exerts some kind of flame-retardant action can be deduced from the relatively low flammability of polymers containing this halogen chemically bound in their structure. The chemical nature of the environment surrounding the bonded chlorine is very important as is apparent from plots of limiting oxygen indices of chlorinated polyethylenes and polypropylenes against the chlorine content (Fig. 1).²⁶⁻²⁹ When the chlorine atom is attached to a tertiary carbon atom, as in polypropylene, a large flame-retardant effect is found at very low levels of chlorine (0-5 wt %; slope 2.0). When the chlorine is attached to secondary carbon atoms, as in chlorinated polyethylene, in chlorinated alkanes used as additives incorporated into polyethylene, in poly(vinyl chloride) or in poly(vinylidene chloride), the flame retardant effect is much smaller. There is also a clear change of slope, so that at low loadings the chlorine is much less effective (slope 0.2) than at high loadings (slope 1.0). The change in slope occurs at a chlorine level which would roughly correspond to a structure such as C₄H₇Cl. For comparative purposes the limiting oxygen index of Penton (a chlorinated polyether with chlorine attached to primary carbon atoms and with the following structural formula



is plotted in the same Figure. It can be seen that the LOI is much smaller than that where the bond is to a secondary carbon atom. This strongly suggests that the mechanism of action is predominantly chemical. When hydrogen chloride or chlorine have been added to the oxidising atmosphere above burning polyethylene²⁶ and polypropylene²⁹ and found to have virtually no effect, the inference has clearly been that the action is confined to the condensed phase. Comparative studies of the LOI and of the limiting index when the oxidising gas is nitrous oxide (LNOI) have shown both curves to be parallel,²⁷ again suggesting no gas-phase effect.

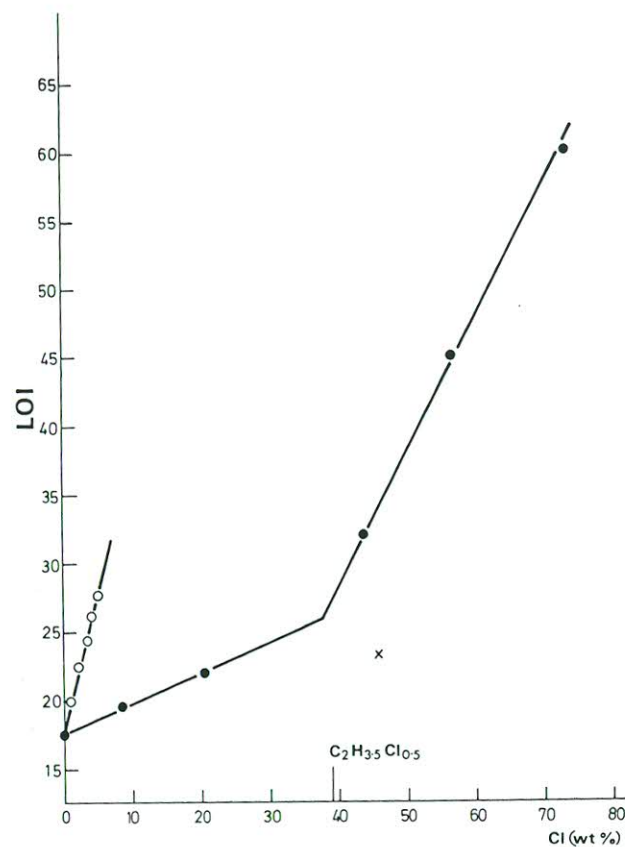


FIG. 1. Effect of chlorine, present in polymers, on their flammability: ○ polypropylene; ● polyethylene, poly(vinyl chloride) or poly(vinylidene chloride); × Penton. (Data taken from refs. 26–29.)

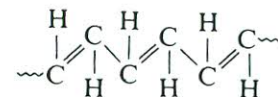
It has traditionally been assumed that chlorinated additive flame retardants act by virtue of their ease of elimination of hydrogen chloride.³⁰ This is borne out by the finding that, e.g. for polypropylene, aliphatic chlorinated hydrocarbons are ineffective flame retardants; their decomposition is so fast that they evolve hydrogen chloride during processing of the polymer.³¹ Analogously chlorinated biphenyls or biphenyl ethers have a very strong Cl—C bond so that their decomposition is too slow to be effective. Thus compounds such as perchloropentacyclodecane with intermediate Cl—C bond strengths are found to be the most useful flame

retardants for this polymer.³¹ In general, aromatic chlorine-containing compounds are said to perform poorly as additive flame retardants,³² although little evidence is found in the literature for this statement. Thermogravimetric studies of the decomposition of liquid and solid chlorinated alkanes frequently used as flame retardants have shown that hydrogen chloride is in fact evolved, at least in the absence of polymer.^{33,34} This suggests that HCl is later effective as a gas-phase flame inhibitor. Thus the flame chain-carriers would react with HCl and transform reactive radicals into relatively unreactive ones such as chlorine atoms. The mechanism of this action will be discussed more fully in conjunction with brominated flame retardants. Hydrogen bromide is a very efficient flame inhibitor, e.g. for polypropylene some five times more so than hydrogen chloride (on a molar basis).²⁹ When additive flame retardants containing chlorine are compared with their brominated analogues, in terms of their efficiency in reducing the LOI of polypropylene, the relative slope values are less than or equal to 2.2.²⁹

It can thus be concluded that, although there may be some gas-phase action for chlorine compounds, it is relatively inefficient and the bulk of the flame-retardant effect takes place in the condensed phase.

An alternative theory^{35–38} has been proposed which assumes the operative mechanism to be a purely physical dilution of the flammable mixtures or a 'blanketing' of the flames by volatile chlorinated species. This mechanism would explain the action of the large number of inorganic chlorides and oxychlorides used, particularly for cellulosic materials. These additives are usually hygroscopic and thus liberate non-flammable gases including HCl.

Before studying other flame retardant elements, it is of interest to look at the mechanism of combustion of the most important chlorinated polymer: poly(vinyl chloride) (PVC). It decomposes principally by a chain-stripping process liberating hydrogen chloride, so that a polyenic residual structure remains:

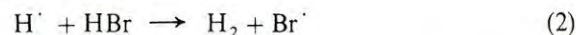
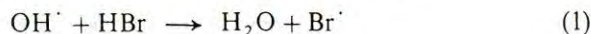


This dehydrochlorinated charry residue can be cyclised to yield benzene, a process which occurs intramolecularly and not intermolecularly.³⁹ It is also possible for some main-chain C—C scissions to occur and small C₂ and C₃ products to be formed which later yield carbon oxides as the sole oxygenated products. The formation of the char and of the aromatic

products is the reason why combustion of PVC produces large amounts of smoke.

5. BROMINE

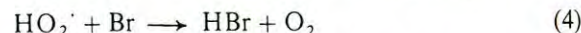
The most widely accepted mechanism for the action of bromine-containing compounds as flame retardants involves the release of volatile species, mainly hydrogen bromide, into the gas phase, where it then inhibits the flame reactions.^{30,32,40-48} Hydrogen bromide is produced by the thermal decomposition of many organic bromine compounds; it thus interacts with the highly reactive free radicals which are the chain carriers responsible for the propagation of combustion, e.g. by reactions 1 and 2.



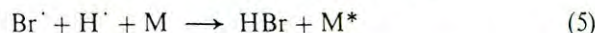
The bromine atoms formed are relatively unreactive but can still eventually abstract hydrogen from the polymeric fuel or its combustible decomposition products (RH) to regenerate hydrogen bromide by reaction 3.



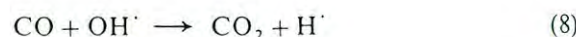
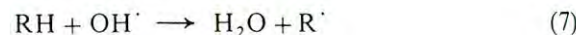
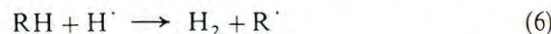
Hydrogen bromide may also be regenerated by termination reactions, either by the bimolecular reaction 4 at relatively low temperatures,⁴⁷



or by the termolecular reaction 5, involving a 'third body'.⁴⁵



This mechanism reduces the concentration of the oxidising hydroxyl radicals and inhibits the normal flame reactions 6 and 7 as well as the subsequent oxidation of CO to CO₂ (reaction 8). In the case of gaseous



premixed flames, this mechanism, or some slight variation, is well established.⁴⁰ Unfortunately, however, the flames above burning polymers are not premixed, although the presence of oxygen very near the surface of

some polymers, such as polypropylene,^{20,21} and of inert gases from the atmosphere in the pre-flame region of burning poly(methyl methacrylate)⁴⁹ means that polymer flames may not be purely diffusional. The amount of bromomethane needed to extinguish pure diffusion and premixed flames has been found to be the same.⁴¹ It is therefore reasonable to assume that, although very few studies have been made of diffusion flames, polymer flames may be very similar to fuel-rich premixed flames.⁴⁷

This simple chemical mechanism suffers from the disadvantage that it does not take into account the well-known fact that, for many organic fuels, the concentration of inhibitor needed to extinguish a flame is much greater when the halogenated compound is introduced from the fuel side rather than from the oxidant side.^{41,50,51} Any bromine introduced directly into a polymer should thus be assumed to be fairly ineffective as compared with the presence of HBr in the gas phase. In fact, however, considerable evidence suggests that the bromine present in the condensed phase which is then volatilised as hydrogen bromide has a much greater effect on flammability than if it were introduced, as hydrogen bromide or as bromine, into the gas phase from the start. For example, although it has been calculated that almost 50 wt % hexabromocyclohexane should be required to confer flame retardance on polystyrene,⁵¹ it has been found experimentally that *ca* 2% is sufficient.⁵² These discrepancies have been attributed to simple failures in the application of the appropriate aerodynamic corrections⁵³ but it may also be that the premixed character of polymer flames is much greater than is generally assumed.

It has been shown that, in the combustion of brominated polystyrenes,⁵¹ brominated polyurethanes,⁵⁴ brominated polyethylene and polypropylene^{31,55,56} and polyesters containing additive brominated flame retardants,⁵⁷ the evolution of hydrogen bromide is an essential initial step. The rate of formation of hydrogen bromide is dependent on the C—Br bond strength, as is indicated by the difference between the efficiencies of *o*- and *p*-bromostyrene comonomers in conferring flame retardance on unsaturated polyesters.⁵⁸ It is therefore to be expected that aromatic bromine compounds, which cannot easily split off HBr, would be much poorer flame retardants than aliphatic compounds. It has been claimed repeatedly that the liberated hydrogen bromide affects in some way the mechanism of the thermal decomposition of the polymer in the condensed phase; this is not yet altogether established. Bromine chemically incorporated into the condensed phase of polyethylene has no effect on the rate of mass loss of the polymer (Fig. 2) nor on the limiting pressure change (Fig. 3) during thermal oxidation.⁵⁶ It does, however, decrease the pressure

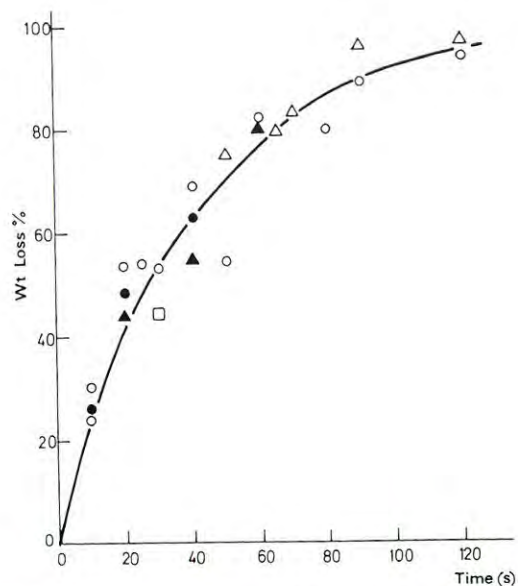


FIG. 2. Effect of chemically incorporated bromine on the rate of weight loss of polyethylene during oxidation: temperature 703 K; atmosphere 5.3 kPa O₂ + 21.3 kPa N₂; sample weight 6.4 mg; ○ untreated polymer; ● Br content 1.7 wt %; △ Br content 2.2 wt %; ▲ Br content 2.6 wt %; □ Br content 6.6 wt %. (After ref. 56, reproduced by permission of The Royal Society and of Professor C. F. Cullis.)

change during the initial stages of the reaction. When, on the other hand, hydrogen bromide is added to the oxidising atmosphere, it decreases the rate of mass loss of the polymer.⁵⁹ Simultaneously, HBr also increases the pressure change during the initial stages of the thermo-oxidative decomposition, so that the erstwhile limiting value is reached much more rapidly, and thereafter it decreases the accompanying pressure change (Fig. 3). These findings, coupled with the fact that virtually all the hydrogen bromide can be recovered from the gas phase after a very short time, suggest that the inhibition reactions do occur mainly in the gas phase. The effects on pressure change are consistent with a rapid elimination of hydrogen bromide, which then leaves 'weak' positions in the main polymer chain, so that 'random' chain scission now occurs principally at these bonds. In this way, rather high molecular weight and relatively involatile products will be formed initially. These compounds will subsequently decompose further and form the same products which would have originated from polyethylene in the absence of bromine, i.e. low molecular weight alkanes

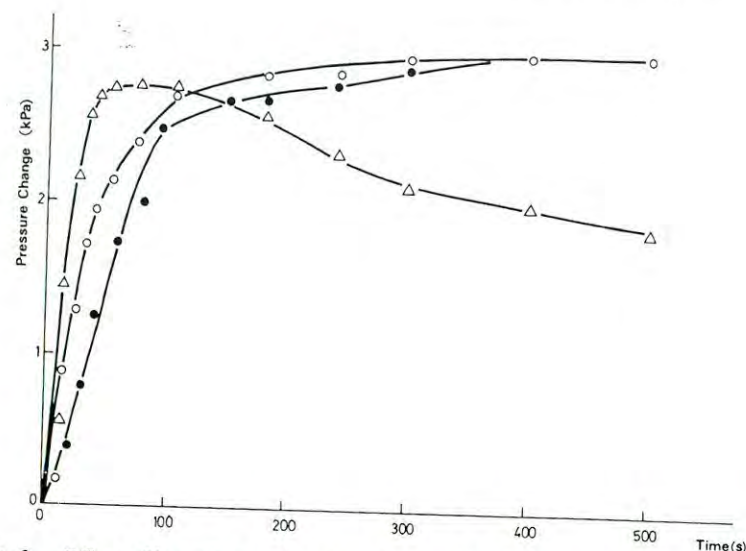
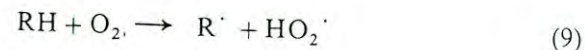


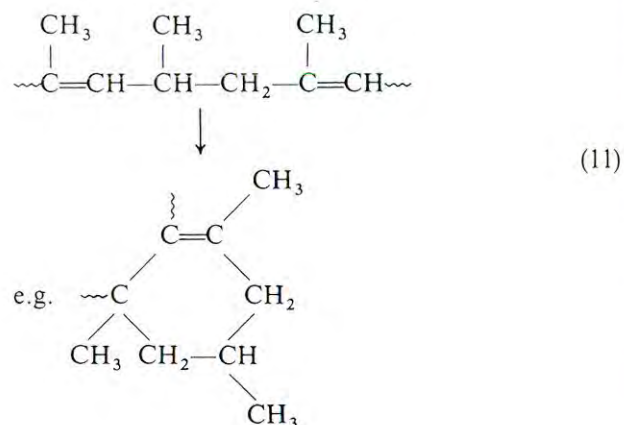
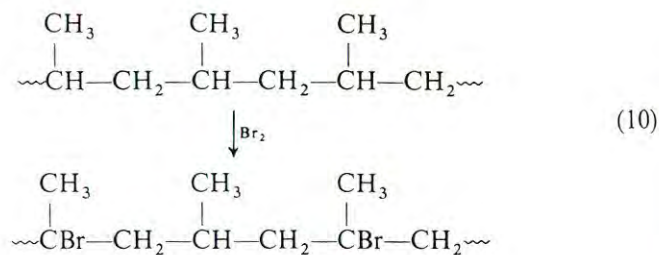
FIG. 3. Effect of bromine on the pressure change accompanying the oxidation of polyethylene: temperature 703 K; sample weight 6.4 mg; ○: atmosphere 20.0 kPa O₂ + 6.6 kPa N₂, untreated polymer; ●: atmosphere 20.0 kPa O₂ + 6.6 kPa N₂, polymer containing 12 wt % Br; △: atmosphere 20.0 kPa O₂ + 5.3 kPa N₂ + 1.3 kPa HBr, untreated polymer. (After ref. 56, reproduced by permission of The Royal Society and of Professor C. F. Cullis.)

and alkenes. When HBr is already present in the gas phase, it is likely to contribute to an initial attack on the polymer chain and produce scissions which lead to gaseous products in addition to those formed by the reaction of the fuel with oxygen (reaction 9).



These reactions will soon be inhibited by the mechanism proposed earlier, so that the pressure rise decreases, i.e. there is inhibition of the flame reactions. No important condensed-phase effect can be attributed to gaseous HBr for this polymer. For polypropylene, however, gaseous hydrogen bromide accelerates thermal decomposition in inert atmospheres,⁵⁵ but not thermo-oxidative decomposition,⁵⁶ so that oxygen must react with the polymer in the condensed phase. In this same polymer, the initial pressure rise due to bromine incorporated by bromination of the substrate is identical to that of the unbrominated sample but the pressure eventually reaches a lower limiting value. This can be interpreted by

assuming that bromination occurs predominantly at the tertiary carbon atoms (reaction 10) and that these positions will be less 'weakened' by the elimination of HBr because of the positive inductive effect of the methyl group. The resulting polymer, however, after elimination of HBr, will be more susceptible to cyclisation reactions typical of polydienes (reaction 11) and will thus give rise to fewer molecules of volatile products.



Other studies have shown that it is only the bromine content and not the type of additive which is relevant to the degree of flame retardance conferred on polyesters,⁶⁰ poly(methyl methacrylate) and polystyrene⁶¹ (Fig. 4). Many halocarbons, such as CF_3Br or $\text{C}_2\text{F}_4\text{Br}_2$, are extensively used as fire suppressants,^{62,63} although they are in fact thermally very stable. In a $\text{CF}_3\text{Br}-\text{CO}-\text{H}_2-\text{Ar}$ flame, hydrogen bromide appears before bromine atoms,⁶⁴ but normally it is difficult to find reactions leading to the formation of HBr from these compounds; they are however much more efficient flame suppressants than HBr itself.⁴⁵ To explain this mode of action it may be useful to consider an alternative purely physical

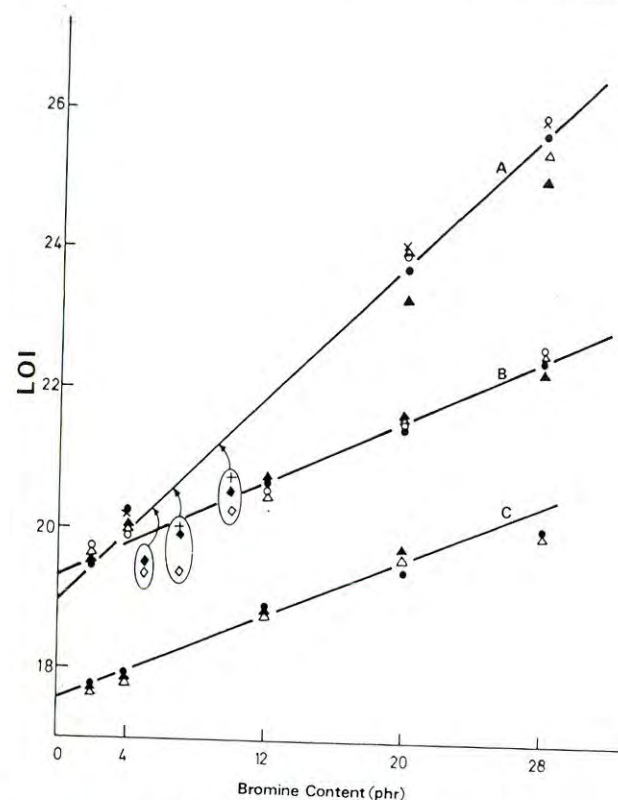


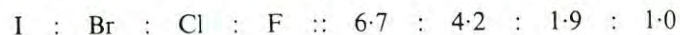
FIG. 4. Effect of bromine additives on the flammability of organic polymers: ○ tetrabromoxylene; ● 1,1,2,2-tetrabromoethene; △ tetrabromoethane; ▲ pentaerythrityl tetrabromide; × tetrabromobutane; + bis(2,3-dibromopropyl) ether; ◇ tribromoneopentyl alcohol; ◆ decabromobiphenyl ether. A, unsaturated polyester resin; B, high impact polystyrene; C, poly(methyl methacrylate). (After refs. 60 and 61, reproduced by permission of Heyden & Son Ltd.)

theory.³⁵⁻³⁸ On re-examination of literature data, it was found that the peak effectiveness of halogen-containing organic compounds acting as flame retardants was dependent on a minimum weight of halogen of *ca* 70% in the fuel-additive mixture.

$$k = \frac{\text{wt halogen}}{\text{wt fuel} + \text{wt flame retardant}} \times 100 = 69.8 \pm 3.5$$

This percentage was found to be completely independent of the nature of

the halogen present, so that all four halogens would then have a relative effectiveness which is in direct proportion to their atomic weights, i.e.



This theory assumes that the principal role of the halogens is to increase the total mass of material that must be introduced into the gas phase per unit time, without at the same time producing an increase in the heat flux back from the flame to the polymeric fuel.³⁸

The effectiveness of halogens, particularly bromine, as flame retardants appears to be enhanced by free-radical initiators.⁶⁵ It was in fact later shown that the action of the free-radical initiators was quite independent of that of the bromine.^{66,67} The free radicals promote depolymerisation of the polymeric fuel which then melts and drips away, taking with it a large proportion of the heat evolved. There is thus no real combined effect of the free-radical promoters and bromine.

Nitrogen does increase the effect of bromine, as for example when ammonium bromide is used as an additive,⁶⁸ or when brominated alcohols are incorporated into polyurethane foams.⁵⁴ The elimination of HBr usually occurs via the formation of an electron-deficient centre. The electron-rich nitrogen atom can act as a nucleophile and stabilise the resulting intermediate structure, thus increasing the ease of elimination of hydrogen bromide.

It can be concluded that, although there may be some effect on the condensed-phase decomposition of the polymer, bromine probably acts mainly by a free-radical mechanism in the gas phase.

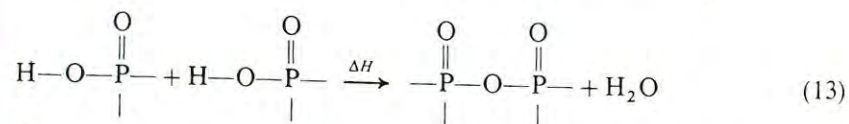
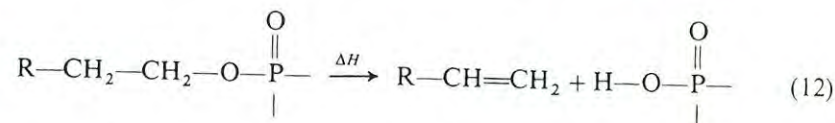
6. PHOSPHORUS

6.1. General

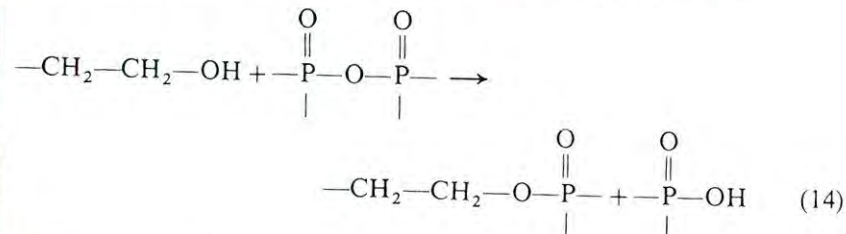
Phosphorus is one of the elements, the flame-retardant action of which is most difficult to understand. Different phosphorus compounds, or indeed even the same phosphorus compound in association with different polymer substrates, may exert modes of action ranging from condensed-phase to gas-phase and from physical to chemical mechanisms.

6.2. Hydroxylated Polymers

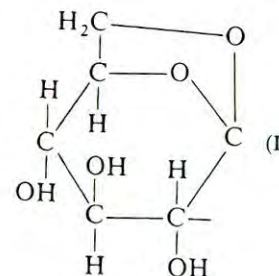
The most carefully studied systems are those where the substrate is cellulose. Phosphoric acid and its esters decompose thermally yielding polyphosphoric acids (12) and water (13).



These reactions are followed first by substitution of the free hydroxyl groups in cellulose by phosphate groups and the concurrent regeneration of phosphoric acid (reaction 14) and finally by dehydration of the resulting organic phosphates to yield an alkenic structure by reaction 12.



Account should be taken of the fact that cellulosic polymers usually decompose by two parallel routes. One of these involves depolymerisation to yield *laevo*-glucosan (I), which, in turn, breaks down to give flammable gaseous products. The other mechanism is a chain-stripping reaction



whereby the substituents on the carbon chain, mainly hydroxyl groups, are eliminated, as water, and the residue becomes an unsaturated char which smoulders or glows instead of undergoing flaming combustion. Thus, if phosphorus-containing flame retardants act by a condensed-phase mechanism such as that proposed, an increase in the amount of char would be expected. This in fact happens with cellulosic polymers.^{69,70}

Simultaneously, however, water must be evolved. This has been shown to act, in the gas phase, to decrease the heat liberated during combustion.⁷¹ Plots of the limiting oxygen index (LOI) against phosphorus content for phosphoric acid-treated cellulose have the same slope as those for the limiting nitrous oxide index (LNOI).⁷² This suggests, then, that the effect of the water produced by reaction of phosphoric acid and cellulose, even if it occurs in the gas phase, is purely physical and will not be affected by a change in the nature of the gaseous oxidant. Further evidence in support of chemical action in the condensed phase comes from the fact that, as the level of phosphoric acid is increased, there is a steady decrease in the temperature at which the endothermic decomposition of cellulose occurs⁷³ (Fig. 5). Phosphoric acid is shown to introduce an additional stage, which is probably the phosphorylation of the hydroxyl groups in cellulose.

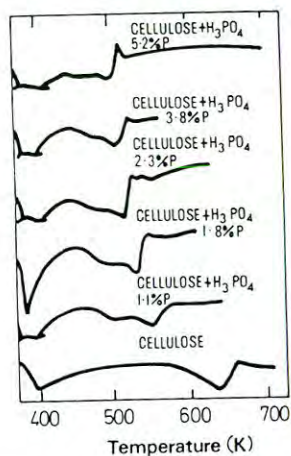


FIG. 5. Thermal analysis of cotton fabrics treated with increasing amounts of phosphoric acid. (After ref. 73, reproduced by permission of John Wiley & Sons Ltd.)

Work carried out on the thermal decomposition of other hydroxylated polymers shows that phosphorylation accelerates also the chain-stripping process as a result of the dehydration and formation of conjugated double bonds; in consequence the scission of polymer chains is inhibited.^{74,75} The differential thermal analysis curves for poly(vinyl alcohol) and for the same polymer after phosphorylation (Fig. 6) show the various changes which phosphorus has produced in the rate of thermal degradation of the polymer, e.g. in the activation energies for the various steps.⁷⁴

The mechanism of this mode of flame-retardant action by phosphoric acid and its esters on hydroxylated polymers is probably ionic, since it is a well-established fact that the hydroxyl groups in cellulose are extensively attacked by acidic catalysts, while they are not affected by neutral salts.¹⁰ Acid catalysts can also induce scission of one of the two C—O bonds in epoxides. A further confirmation of this mechanism is therefore provided

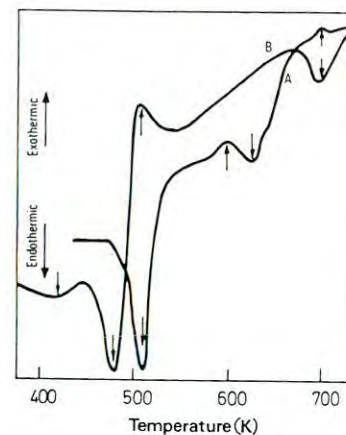


FIG. 6. Thermal analysis of poly(vinyl alcohol) (A) and phosphorylated poly(vinyl alcohol) (B). (Reproduced from ref. 74, by permission of the publishers, IPC Business Press Ltd ©.)

by the fact that studies of the LOI and LNOI of epoxy resins have shown that triphenyl phosphine does not chemically affect the gas-phase flame reactions: triphenyl phosphine produces only condensed-phase effects on the decomposition of these resins.⁷⁶ Epoxy coatings, modified with phosphorus esters, show an increased char-forming tendency and intumescence,⁷⁷ also signs of condensed-phase reactions.

The effect of phosphorus on the flame retardance of cellulosic compounds is considerably enhanced by nitrogen bases, such as urea, guanidine or dicyanodiamide. One of the main advantages of the use of nitrogen is the clearly increased ease of attachment of the phosphorus to the polymeric fabric. This reduces loss of the additive due to its solubility in water. There is abundant evidence that the minimum amount of phosphorus needed to make cotton flame-retardant decreases with increasing amounts of nitrogen.^{78,79} It is not clear whether this is simply an effect of the better durability of the phosphorus finish, or whether it is an

additive or even synergistic effect.⁹ The most pronounced effects have been found with nitrogen compounds containing relatively non-basic N—H groups.⁷⁹ The flame-retardant action is dependent, however, on various factors, such as the mode of application of the phosphorus and nitrogen compounds.⁸⁰ A systematic study was undertaken of nitrogen bases added to a cellulose-triphenyl phosphate system.⁸¹⁻⁸² The char yields obtained increased with nitrogen content. The nitrogen compounds were also shown to interact exothermically with *laevo*-glucosan in a manner similar to that in which acids act. Transphosphorylation takes place and it was concluded that phosphoramides were formed as intermediates. The nitrogen compounds thus probably act by a nucleophilic attack on the phosphate, which results in the formation of numerous P—N bonds.⁷² These bonds, being more polar than the original P—O bonds, result in increased electrophilic character of the P atom and the rates of acid-catalysed dehydration of cellulose are thus also higher. In this way char formation is increased at the expense of that of flammable *laevo*-glucosan. When various phosphoramides are used directly as additives, the slopes of the plots of the proportion of cellulose converted into char ($Y(1-X)$), against the logarithm of the phosphorus content, are all the same, irrespective of N content, while the slope for phosphoric acid is much smaller (Fig. 7).⁸³ When a phosphoramide is cross-linked with a melamine resin, the slope still does not change but the effect is much larger. This is due to a physical rather than chemical cause: the volatility of the phosphoramide is decreased and thus more of the reagent is in contact with the cellulose during the pyrolysis. When the amido group is replaced by a methyl ester (not containing nitrogen) or by a nitrile (which is non-nucleophilic and cannot, thus, form P—N bonds), the resulting slope is the same as that for phosphoric acid. This tends to give support to the mechanism proposed.

Summing up, then, phosphorus compounds confer flame retardance on hydroxylated polymers, by a condensed-phase esterification of the hydroxyl groups as a result of acid catalysis. Water is then liberated which acts as a physical agent in the gas phase. The incorporation of nitrogen which can form P—N bonds increases the effectiveness of the esterification process.

6.3. Other Polymers

In the case of thermoplastic polymers, a significant proportion of the phosphorus added is lost by volatilisation prior to the breakdown of the polymer itself, so that evidently any condensed-phase action is relatively small.⁸⁴ Phosphorus-containing compounds are known to be gas-phase

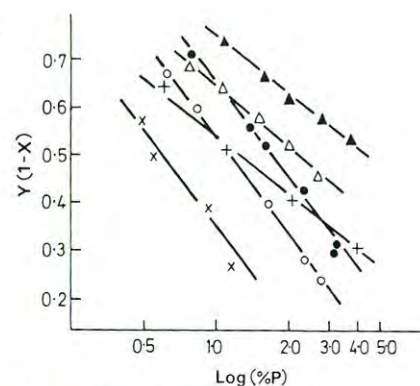
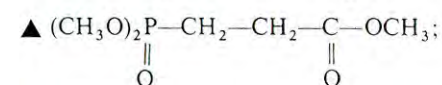
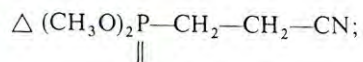
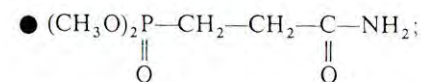
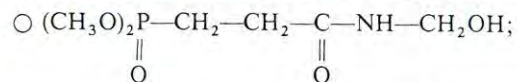


FIG. 7. Effect of different phosphorus-containing additives on the proportion of cellulose converted into char ($Y(1-X)$). Additives:



× $(\text{NHCH}_3)_3\text{P}=\text{O} + \text{melamine};$ + $\text{H}_3\text{PO}_4.$ (After ref. 83, reproduced by permission of the Swiss Federations of Dyers and of Chemist-Colourists and of Professor R. H. Barker.)

flame inhibitors,⁴⁷ and this is confirmed by the finding that various non-halogenated phosphorus compounds with the phosphorus in different oxidation states have roughly the same effect on the LOI of polyethylene,²⁷ and of poly(ethylene terephthalate) (PET).⁸⁵ The mechanism of action may involve the formation of heavy vapour clouds which effectively 'smother' the flame by excluding oxygen.⁸⁶ During the combustion of polystyrene⁸⁶ and of poly(ethylene terephthalate),⁸⁷ for example, most of the phosphorus is volatilised and almost none remains in the solid residue.

Tricresyl phosphate, which increases the limiting oxygen index of several thermoplastic polymers (polyethylene, polyoxymethylene, poly(methyl methacrylate)) to similar extents (8–15%), has a much greater effect on the LOI of poly(ethylene oxide) (+40%).²⁷ This is an indication of the importance of the substrate. Poly(ethylene oxide) is amenable to acid catalysis due to the presence of the ether oxygen atom and its rate of

decomposition is therefore probably affected by phosphorus in the condensed phase. The other polymers are, however, affected only as a result of effects on the gas-phase reactions of their decomposition products.

The combined action of phosphorus and nitrogen on the combustion of thermoplastics is occasionally antagonistic: this is the case with polymers such as polyethylene, polypropylene and poly(methyl methacrylate).⁹ This can be explained if the acidic phosphate species changes the pattern of breakdown of poly(methyl methacrylate) (PMMA) so that it suffers chain-stripping, instead of depolymerisation to monomer, and thus yields large proportions of char.⁸⁸ The addition of nitrogen bases would then decrease the effectiveness of this catalytic action. In fact, however, in blends of PMMA with ammonium polyphosphate, no reaction occurs between the two components of the blend, but the organic polymer reacts with polyphosphoric acid, the breakdown product of its ammonium salt.⁸⁹ This chemical explanation of P-N antagonism is inconsistent with the mechanism of action proposed for thermoplastic polymers, which is mainly physical and takes place in the gas phase.

Phosphorus-based flame retardants are fairly extensively used in many nitrogen-containing polymers such as polyacrylonitrile,⁹⁰ natural⁹¹ and synthetic⁹² polyamides and polyurethanes,⁹³ but the mechanism of action is not yet well understood.

Studies of the combined action of phosphorus and halogens on the combustion of polyesters and polyurethanes have shown that the reaction occurs mainly in the condensed phase.^{87,94-96} There is, generally, increased formation of char and a large proportion of the phosphorus remains in the solid residue. The main function of the halogen in halogenated phosphates is probably to prevent the volatilisation of the additive.⁸⁷ Thus, while trihexyl phosphate, which is non-volatile, is just as effective a flame retardant for poly(ethylene terephthalate) as a brominated phosphate, tripropyl phosphate does not significantly affect the LOI of the polymer. It is also interesting that tris(chloromethyl-2-chloroethyl) phosphate is a very much more efficient flame retardant than tris(2,3-dichloropropyl) phosphate, the only significant structural difference between the two compounds being the tertiary carbon atom in the former; this compound is thus less volatile. The suggested mechanism of action in the condensed phase involves an acid-catalysed aldol condensation. Tris(2,3-dibromopropyl) phosphate also acts in the condensed phase when conferring flame retardance on polystyrene, but the mechanism is not yet clear.⁹⁷ Another phosphorus-halogen system widely used, but so far little studied, comprises the phosphate plasticisers for PVC.

TABLE I
EFFECT OF RED PHOSPHORUS ON LIMITING
INDICES OF POLYETHYLENE TEREPHTHALATE

Additive wt (%)	LOI	LNOI
0.0	20.4	46.4
1.0	23.6	47.9
2.0	25.1	48.7
3.0	27.6	49.3
4.0	30.3	49.9
Slope (LI ÷ wt %)	3.57	1.64

(After ref. 100.)

Finally it is of considerable interest to mention a compound which is surprisingly a very effective flame retardant, viz. red phosphorus, a polymeric form of elemental phosphorus which is quite distinct from the more common white P₄ molecules. It is obviously the most economical way in which phosphorus can be made to give maximum yields of the acid catalyst for condensed-phase action. Significantly, in the case of polyurethanes, the action of red phosphorus is enhanced by the presence of small amounts of halogen compounds.^{98,99} Less easy to explain is the combined effect of red phosphorus and halogens for thermoplastic polymers such as polyolefins or PVC.⁹⁹ In the case of poly(ethylene terephthalate), red phosphorus is a very good flame retardant in its own right and it acts partly in the gas phase. This conclusion is confirmed by the

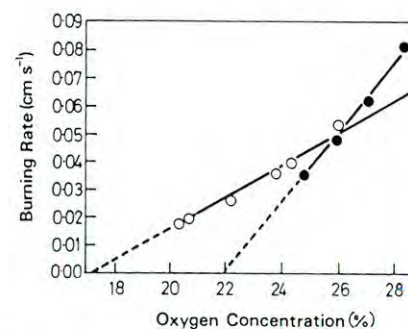


FIG. 8. Effect of oxygen content on the burning rate of poly(ethylene terephthalate): ○ untreated polymer; ● polymer + 2% red P. (After ref. 100, reproduced by permission of John Wiley & Sons Inc.)

different slopes of plots of LOI and LNOI versus phosphorus content, as described by the equation

$$LI_p = LI_0 + \text{slope} \times P^{1/2}$$

where LI_p is the limiting index (LOI or LNOI), at an additive concentration of phosphorus of P wt %, and LI_0 is the same index when no phosphorus has been added¹⁰⁰ (Table 1). The presence of red phosphorus does also affect, however, the rate of burning of the polymer, so that there is probably a considerable proportion of condensed-phase action (Fig. 8).

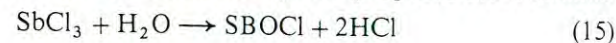
7. ANTIMONY

The use of metal oxides as flame retardants had already been suggested by Sir William Perkin at the turn of the century. It was not, however, until World War II that antimony trioxide began to be used¹⁰¹⁻¹⁰³ and it was soon shown that Sb_2O_3 (or more accurately Sb_4O_6) is generally ineffective in the absence of halogens, a finding borne out by most later studies.^{8,9,68,102-105} In some isolated cases, however, antimony oxide may provide some degree of flame retardance on its own.¹⁰⁶⁻¹⁰⁸ It is however the apparent synergism between antimony and halogens which has been the cause of the wide use of antimony as a flame retardant. The mechanism of action of antimony-halogen systems has been the subject of much research and is the butt of deep controversies. The greatest amount of work has been devoted to the identification of the active species and to the determination of the phase in which the flame-retardant action takes place.

The optimum atomic ratio for the Cl-Sb or the Br-Sb systems can now be safely assumed to be 3:1.^{68,102,105,109} This does not however necessarily imply that volatile antimony trihalide is the active intermediate. The initial assumption made^{102,103} was that antimony oxyhalide was the species responsible for the flame-retardant action. Studies of the thermal decomposition of antimony oxychloride ($SbOCl$)¹¹⁰ do in fact show that this compound decomposes yielding, in three endothermic steps, gaseous antimony trichloride and a solid residue of Sb_2O_3 . The thermogravimetric pattern of decomposition of $SbOCl$ has a substantial overlap with that of various flexible polyurethane foams for which the Sb-Cl system had been shown to be a good flame retardant. Several other flame-retardant systems (or putative flame-retardant systems) were also studied and it was seen that those additives which had considerable thermogravimetric overlap with the foam were effective combustion inhibitors, while those which decomposed

at either substantially lower or higher temperatures than the polymer had little or no flame-retardant action. This led to the conclusion that $SbOCl$ is formed *in situ* and then produces $SbCl_3$, which is the actual flame retardant.¹⁰⁵ Antimony trichloride is too unstable to be incorporated into a polymer and cannot therefore be used as a flame retardant. This means, of course, that the theory cannot be tested directly. There was, however, some earlier evidence for the gas-phase action which was taken as support for this mechanism: thus the limiting oxygen index of chlorinated polyethylene is improved by antimony trioxide but the limiting nitrous oxide index is unaffected.^{26,27}

However, mass spectrometric studies of the flames above polymers containing antimony + chlorine have indicated that there is no $SbCl_3$ in the flame zone,⁴⁷ although solid antimony monoxide (SbO) and even metallic antimony (Sb) can be detected. A sequence of reactions is therefore suggested, including 15 and 16. The active species proposed are thus solid



antimony monoxide and gaseous hydrogen chloride, the inhibitory action being at least partly heterogeneous. Triphenyl stibine is oxidised to SbO , probably explaining why it is effective, in the absence of halogens, in reducing the flammability of epoxy resins.⁷⁶

The fact that at least 50% of the antimony is volatilised from polymers also including halogens,¹¹¹ while 95% of the antimony remains in the solid residue when halogen-free polymers are burnt,²⁷ is further evidence for a gas-phase mechanism.

Thermal analysis of antimony oxide-halogen systems in the absence of an organic polymer provides no evidence for the formation of $SbOCl$, but nevertheless indicates that volatilisation of chlorine and antimony^{33,34,112-114} and indeed of bromine and antimony^{33,112-114} occurs in a 3:1 ratio. This does not, however, appear to be the complete solution of the mechanistic problem. Thus, for instance, the synergistic effect of Sb_2O_3 is much larger with solid chlorinated waxes than with liquid compounds with the same chlorine content.^{33,112-114} This can be explained by the fact that the temperatures of decomposition of the solid additives to form HCl are much lower than their temperatures of volatilisation. The liquid additives on the other hand distil unchanged and do not decompose until fairly high temperatures are reached (Fig. 9). Antimony oxide can affect the rate of formation of volatile products (V) from the chlorinated additives and the Sb-Cl systems can alter V for the polymeric substrate. When

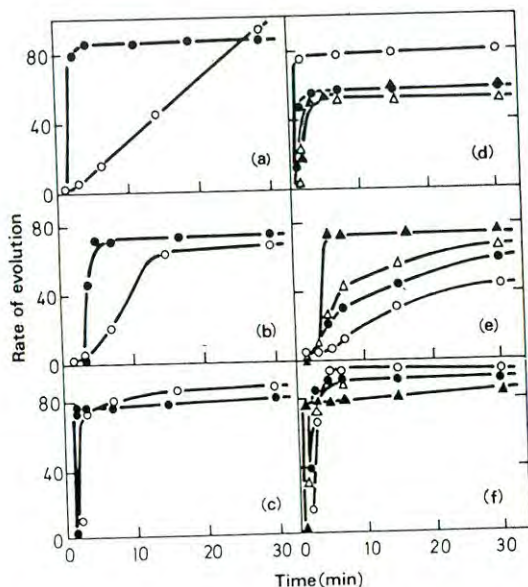


FIG. 9. Rate of formation of gaseous products from various mixtures of polyester, chlorinated paraffins and antimony trioxide: (a) ○ Dechlorane 4070; ● Dechlorane 4070 + Sb_2O_3 (at 683 K); (b) ○ Cereclor 70; ● Cereclor 70 + Sb_2O_3 (at 583 K); (c) ○ Cereclor 70; ● Cereclor 70 + Sb_2O_3 (at 683 K); (d) ○ Cereclor 70 + Sb_2O_3 ; ● Cereclor 70L + Sb_2O_3 ; △ Cereclor 65L + Sb_2O_3 ; ▲ Cereclor S52 + Sb_2O_3 (at 583 K); (e) ○ polyester; ● polyester + 15 wt % Sb_2O_3 + 15 wt % Cereclor 70 (incorporated into the substrate); △ polyester + 15 wt % Sb_2O_3 + 15 wt % Cereclor 70 (physically mixed with the substrate); ▲ Cereclor 70 + Sb_2O_3 (at 583 K); (f) as in (e), but at 733 K. (After ref. 33, reproduced by permission of Dr. G. S. Learmonth.)

different chlorinated paraffins are compared, a much higher temperature is required for a significant increase in the case of the liquid Dechlorane 4070 than for the solid Cereclor 70; for some liquid additives the rate always remains very low. The Sb-Cl system increases V for the polymer if the experiment is carried out at a temperature below the ignition point of the resin (723 K), while it decreases V at a higher temperature when enough flammable products would otherwise be formed from the polymer for ignition to occur. Analysis of the thermogravimetric curve of the polymer shows that the second stage of its decomposition, i.e. that in which the unsaturated polyester resin gives off most of the volatile products, is the one most affected. This is clear evidence for condensed-phase action, which probably occurs before the gas-phase reactions.

The antimony-halogen system has been found to enhance the condensed-phase formation of char, which then insulates the bulk of the polymer by the formation of a physical barrier.^{32,115} Although the difference in thermal dehydrochlorination rates of chlorinated polyethylene in the presence and in the absence of antimony trioxide can be attributed to a condensed-phase reaction,¹¹⁶ the opposite conclusion can be drawn from the lack of effect of Sb and Cl on the thermal decomposition of polypropylene in nitrogen.¹¹⁷

The system chlorinated paraffins + Sb_2O_3 is very much less effective in reducing the extinction times of glass-reinforced polyester resins than pentabromotoluene (PBT) with Sb_2O_3 .¹¹⁸ If, however, even a small proportion of PBT is added to the chlorine-containing system, an effect is found which is as large as that of PBT- Sb_2O_3 system. This has led to the interpretation that the mechanisms of action of antimony oxide with bromine and with chlorine are qualitatively different.

In conclusion, it now seems probable that some reaction takes place in the condensed phase to produce the antimony trihalide, via the intermediate formation of a Lewis acid.¹¹⁹ The use of Friedel-Crafts alkylation reagents in conjunction with an antimony oxide-chlorine Lewis acid precursor has, in fact, been shown to promote *in situ* charring of polystyrene.¹²⁰ It is however important that the halogen compound for the Sb-halogen system is one that does not volatilise prematurely. If this happens, the polymer structure would in fact be weakened and its flammability increased.^{111,121} Once antimony halide is formed, it volatilises and breaks down rapidly in the hot pre-flame zone to produce SbO and hydrogen halide, which are the active species reaching the flame zone. It is probably the existence of the additional heterogeneous scavenging action of SbO , reminiscent of the effect of lead oxide formed from lead alkyls added to motor gasolines, that is the key factor which allows the drastic reduction in the proportion of halogen required to render a polymer flame-retardant.

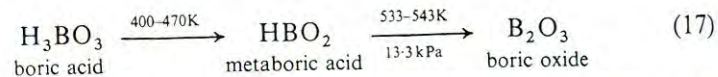
8. BORON

Four different mechanisms of action can be attributed to additives containing boron:

- (a) Formation at the surface of the solid polymer of 'glassy' inorganic deposits which act in a similar fashion to intumescent coatings.

- (b) Enhancement, with hydroxylated polymers, of char production at the expense of the formation of flammable gaseous products; this involves a condensed-phase mechanism whereby the boron-containing compound is first converted into boric acid and subsequently forms borate esters.
- (c) Release of water vapour into the gas phase by hydrated boron compounds (or of ammonia by ammonium borates); the water released acts both as a heat sink, reducing the amount of heat transferred back to the polymer for its continued decomposition, and as a diluent of the gaseous fuel, thus removing the composition and temperature of the gaseous mixture from within the flammability limits.
- (d) Chemical inhibition of oxidation reactions at the gas-solid interface by acting as free-radical scavengers.

Boric acid and its hydrated salts were among the first inorganic compounds to be used as flame retardants for cellulosic textiles.² They have low melting points and their thermal decomposition occurs according to the general scheme 17:⁸



Boric oxide becomes 'glassy' at *ca* 600 K and starts flowing above 775 K. The mixture of boric acid and borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), which has very little tendency to crystallise out, starts losing water of hydration when contained in a cellulosic polymer at a temperature intermediate between that of the softening point of the polymer and that at which extensive thermal decomposition starts. The inorganic residue traps part of the evolved water and a portion of the polymer will expand so as to produce a surface layer which is similar to an intumescent coating and which insulates the bulk of the polymer from the external heat source. Borax, in the absence of boric acid, is an excellent inhibitor of flaming combustion, but is a catalyst for the afterglow of char residues.¹²² This is very symptomatic because it has been found that, for cellulose, the borax added is not uniformly distributed throughout the polymer but tends to remain near the surface.¹²³ Boric acid is normally thought of as a rather poor flame retardant, which is however very effective in suppressing glowing combustion. This may be a misconception because the efficiency of boric acid in increasing the limiting oxygen index and limiting nitrous oxide index for wool passes through a maximum at *ca* 0.5 wt % of boron, while no such

effect is found for borax, a boric acid-borax mixture or ammonium fluoroborate (Fig. 10).¹²⁴ In none of these cases is there an apparent chemical effect in the gas phase since the LOI and LNOI vary in a similar fashion. The borax-treated wool melts and chars while no melting is observed for the boric acid-treated samples. The action of the fluoroborate has been attributed to the action of liberated boron trifluoride in the gas phase⁶⁸ and to a dehydration and cross-linking mechanism similar to that of borax. The results on wool tend to suggest, however, that neither

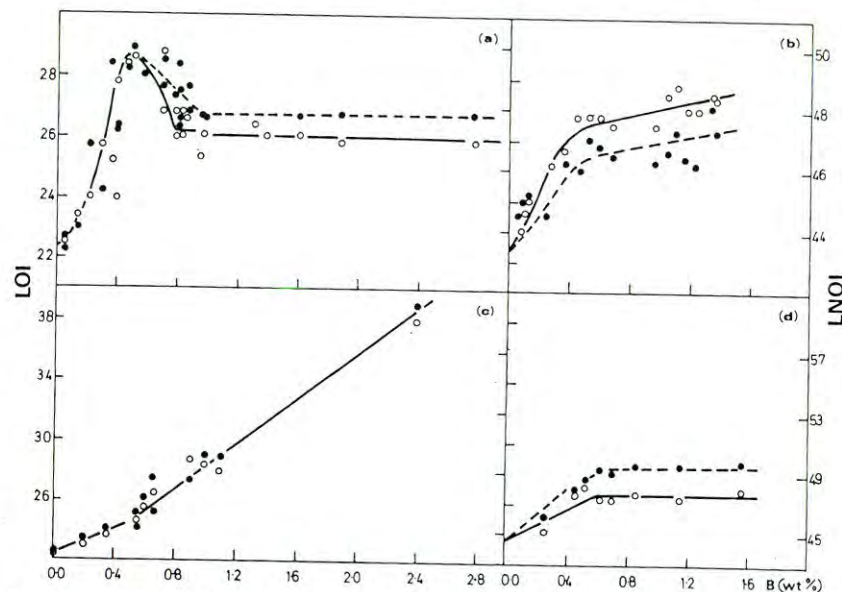
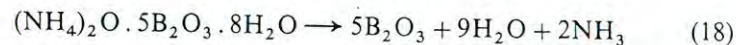


FIG. 10. Effect of boron on the flammability of wool: ○ oxidant, O_2 ; ● oxidant, N_2O ; (a) boric acid; (b) borax; (c) ammonium fluoroborate; (d) borax + boric acid (7:3). (After ref. 124, reproduced by permission of the Textile Research Institute.)

mechanism is entirely correct. Several water-soluble borates have been used as flame retardants and are quite effective, their efficiency being largely dependent on the associated cation and on the ratios of metal oxide to boric oxide and of inert gases to boric oxide. In this connection, ammonium salts, e.g. ammonium pentaborate, should be mentioned because they yield additional non-flammable gases (ammonia, reaction 18) which are volatilised instead of depositing metal oxide residues.



The mechanism of char enhancement by borates for hydroxylated polymers is very similar to that exhibited by phosphates: the free hydroxyl groups are esterified, forming borate esters, and this is followed by loss of water.¹²⁵ Thus, in cellulose, char production is favoured at the expense of the formation of *laevo*-glucosan. Hydrated borates are more effective than the anhydrous salts,¹²⁶ so that the release of inert gases also occurs with borate flame retardants. Boron itself remains in the condensed phase, analysis of cellulosic char residues showing that 90% of the boron added has not volatilised.

The temperature at which the flame retardant action occurs (*ca* 535 K) is perfectly adequate for cellulose, which does not start to decompose significantly below 620 K. Another hydroxylated polymer, however, poly(vinyl alcohol), is not a good substrate for borate flame retardants, because it starts to decompose at *ca* 475 K¹²⁷ so that, when boric oxide is formed, the polymeric hydroxyl groups have already been eliminated. Phenolic resins are hydroxylated polymers for which borates are very efficient flame retardants.^{128,129}

Fused boric oxide has been used as a flame retardant for cotton fabrics¹³⁰ and it has been found that smouldering combustion is inhibited only when the source of heat is placed above the material and not when the cellulose is heated from below. The resulting chars have been found to have a free-radical content some 2–3 times lower than those from cotton treated with lithium hydroxide or sodium chloride. This has led to the suggestion that some 'active sites' in the char are blocked chemically by volatile species acting heterogeneously by a free-radical mechanism. If an analogy were sought with other flame retardants, the action of SbO is the one that comes most clearly to mind.

Finally, the action of zinc borates (and some other insoluble borates) deserves mention. They have been extensively used as partial or total replacements for antimony oxide in conjunction with halogens.^{131–133} The mechanism of action is probably different from that of Sb₂O₃ but not much is yet known about it despite the fact that a number of studies have been made. There may be some interaction between the boron and the zinc.

9. ALUMINIUM

Aluminium oxide trihydrate is the flame retardant most abundantly used for plastics during the last few years (representing almost 44% of the total in the United States in 1978¹). This implies a phenomenal rise since hydrated

alumina was introduced only around the mid-1960s as a flame retardant for unsaturated polyester resins, on account of its low cost.¹³⁴

Studies of its effect on the limiting oxygen index of epoxy resins showed that, while anhydrous alumina did not markedly affect this measure of polymer flammability, the hydrated oxide produced a significant increase in the LOI and a parallel one in the LNOI (Fig. 11).⁷⁶ This suggests that the predominant inhibiting action occurs in the condensed phase and involves principally an endothermic dehydration. The alumina thus acts as a heat sink and prevents the flammable gases from reaching temperatures at which they would ignite, while the water vapour released simultaneously dilutes the gaseous fuel.

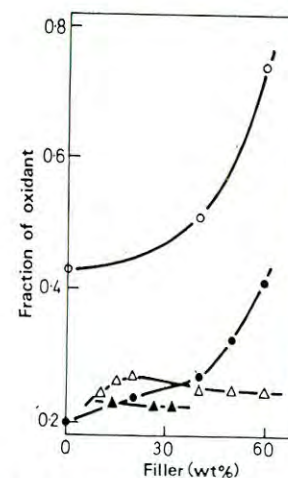


FIG. 11. Effect of alumina on the flammability of epoxy resins: ○ Al₂O₃·3H₂O (oxidant, N₂O); ● Al₂O₃·3H₂O (oxidant, O₂); △ Al₂O₃ (Norton 389001) (oxidant, O₂); ▲ Al₂O₃ (Linde A) (oxidant, O₂). (After ref. 49, reproduced by permission of Dr. C. P. Fenimore.)

These experiments have thus shown that the effect of hydrated alumina does not consist merely in the dilution of the solid combustible polymer by a non-flammable filler material. It thus became of interest to determine the heat that alumina trihydrate needs to absorb to lose its water of hydration. Early measurements of this heat of hydration¹³⁵ suggested a value of 1970 Jg⁻¹,^{136–140} but more recent results^{141–143} indicate that this figure is probably too high and an average value of 1170 Jg⁻¹ has been obtained,¹⁴³ which is almost independent of particle size.^{144,145}

An early source of interest in alumina trihydrate was its effect on smoke.⁷⁶ The hydrated material has a significantly greater effect on the reduction of smoke, as well as on flammability, than is the case for the anhydrous compound,²⁸ although the injection of water as such into the oxidant gases does not affect the amount of smoke produced.¹⁴⁶ Comparison with other fillers (e.g. hydrated silicates) shows that alumina is very much more effective than any of the others in increasing the time to reach a critical obscuration from styrene-butadiene rubber (SBR).¹⁴⁷ If another smoke parameter is analysed, i.e. maximum smoke density, alumina is not much better than other fillers.¹⁴⁷ This suggests that what is occurring is a decrease in the rate of formation of smoke, i.e. the alumina has a chemical effect on the condensed-phase mechanism of thermal decomposition. This is further confirmed by results with other polymers. The distribution of products from burning polystyrene is markedly changed by hydrated alumina, there being, for example, a considerable increase in the amount of toluene formed.¹⁴⁸ Smoke formation is thus decreased as a result of the formation of less smoky volatile intermediate products. In unsaturated polyester resins, the amounts of unburnt hydrocarbons produced are increased and the rate of smoke generation is reduced.¹⁴⁹ This decrease in the rate of smoke formation, even in the presence of smoke-enhancing brominated additives, is, as with SBR,¹⁴⁷ a much more pronounced effect than the decrease in maximum smoke density.

It having been established that alumina probably acts chemically in the condensed phase, its possible interaction with halogens will be considered. Some early evidence for a chemical mode of action has remained largely unnoticed. A combination of 16.8% alumina trihydrate and 3.4% tris(2-chloroethyl) phosphate gives excellent flame retardancy to rigid polyurethane foams,¹⁵⁰ while 20% $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ alone is ineffective in reducing the flammability of both rigid and flexible polyurethane foams.⁹³ Similarly, while the addition of fillers, such as glass fibre or calcium carbonate, increases the burning rates of chlorendic acid-based unsaturated polyester resins, this is not the case for hydrated alumina.¹⁵¹ It has been suggested, albeit without much supporting evidence, that the reduction by alumina of the flammability of SBR rubbers in the presence of chloroparaffins is due to a formation of AlCl_3 which catalyses in the solid phase the elimination of halogen radicals.⁸ Thermogravimetric studies of mixtures of anhydrous alumina with chlorinated wax showed no volatilisation of aluminium chloride.³⁴ This only served to confirm that alumina is unlikely to act in the gas phase. Perhaps more important is the

fact that no apparent effect is found on the thermal decomposition pattern of the chlorowax. The addition of $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ to unsaturated polyester resins treated with a brominated additive was found to decrease the amount of hydrogen bromide liberated into the gas phase, as measured in a smoke chamber (Fig. 12).¹⁴⁹ In other work, samples of acrylonitrile-butadiene-styrene copolymer (ABS) containing decabromobiphenyl and of high density polyethylene (HDPE) containing chlorinated wax, in both cases in

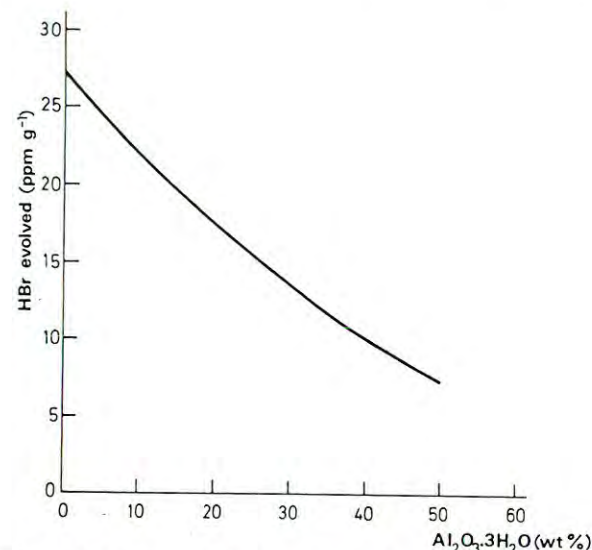


FIG. 12. Effect of alumina trihydrate on the evolution of hydrogen bromide from unsaturated polyester resins. (After ref. 149, reproduced by permission of the Society of the Plastics Institute, Inc., and of Dr. D. P. Miller.)

conjunction with either anhydrous alumina, alumina monohydrate or alumina trihydrate, were heated in the source of a mass spectrometer and the volatile products were analysed.¹⁵² In no case were Al-Cl or Al-Br species found, which is further confirmation that the alumina acts primarily in the condensed phase.

The limiting oxygen indices of ABS treated with decabromobiphenyl (DBB) and with each of the aluminium oxides show very definite signs of synergism (Table 2).¹⁵² The LOI of the polymer containing the mixture is compared, in Fig. 13, with the LOI which would correspond to an additive effect of the flame retardants (LOI_{add}):

$$\text{LOI}_{\text{add}} = \text{LOI}_{\text{Br}} + \text{LOI}_{\text{Al}} - \text{LOI}_{\text{p}}$$

TABLE 2
EFFECT OF DECABROMOBIPHENYL ON THE LIMITING OXYGEN INDEX OF ABS COPOLYMER TREATED WITH ALUMINA

DBB ^a (phr)	LOI		
	Al ₂ O ₃	Al ₂ O ₃ · H ₂ O	Al ₂ O ₃ · 3H ₂ O
0	19.2	18.9	18.8
5	21.5	19.7	19.7
10	22.9	20.9	20.6
15	24.4	21.5	21.4
20	25.8	22.2	22.2
25	26.6	23.1	23.1
30	27.9	23.8	24.2
35	29.5	24.7	25.7
40	30.9	25.3	27.5
45	33.0	25.9	29.0
50	36.4	26.4	30.1
0 ^b	18.6	18.6	18.6

(After ref. 152.)

^a 10 phr alumina added in all cases.

^b No additives.

where LOI_{Br} is the LOI value of the polymer containing bromine, LOI_{Al} is that of the polymer containing Al₂O₃ or Al₂O₃ · 3H₂O and LOI_p is that of the untreated polymer. It can be seen that with ABS a very pronounced synergism occurs between decabromobiphenyl and anhydrous alumina. This is slightly less marked with the trihydrate, where the effect occurs principally at high loadings of Br (Br:Al > 3:1), and is much less noticeable with the monohydrate. An increase in the concentration of metal oxide does not apparently affect the LOI, when the amount of halogen is kept constant (Table 3). With HDPE some synergism is also found between anhydrous alumina and decabromobiphenyl but the effect is much smaller since the individual flame retardants are also much less effective for this polymer. Chlorinated wax does not seem to have any clear-cut synergistic effect with these metal oxides in the case of HDPE. In fact the order of effectiveness of the aluminium oxides is the order of increasing water content, the anhydrous compound being perhaps even slightly antagonistic towards the chlorinated wax.

The results with Al and Br suggest that there may be three mechanisms by which flame retardance may be conferred on the polymer. Until the

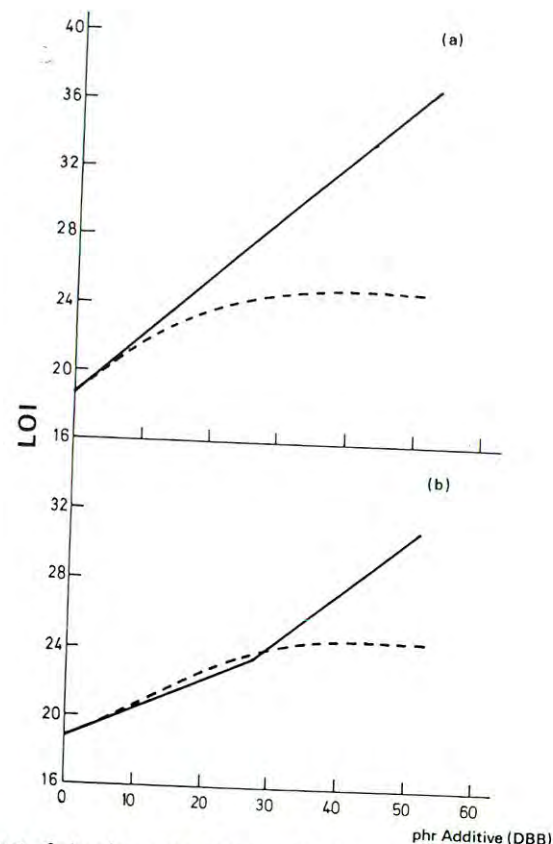


FIG. 13. Effect of alumina and decabromobiphenyl (DBB) on the flammability of acrylonitrile-butadiene-styrene copolymer: — experimental; ---- calculated assuming additive behaviour; (a) Al₂O₃; (b) Al₂O₃ · 3H₂O.

TABLE 3
EFFECT OF ALUMINA ON THE LIMITING OXYGEN INDEX OF ABS COPOLYMER TREATED WITH DECABROMOBIPHENYL

Alumina ^a (phr)	LOI		
	Al ₂ O ₃	Al ₂ O ₃ · H ₂ O	Al ₂ O ₃ · 3H ₂ O
0	20.5	20.5	20.5
10	22.9	20.9	20.6
15	22.9	20.9	20.6
20	22.9	20.9	20.6

(After ref. 152.)

^a 10 phr decabromobiphenyl added in all cases.

bromine content is such that Br:Al > 3:1 with the anhydrous oxide, there is a condensed-phase reaction between Al and Br which probably inhibits the decomposition of the polymer. As the concentration of bromine increases, there is additionally an elimination of hydrogen bromide which acts in the gas phase and thus increases the slope of the variation of the LOI. With the trihydrate, the water of hydration probably partly inhibits the condensed-phase mechanism between Al and Br but exerts a positive overall flame-retardant effect on account of its own direct diluent action. The monohydrated oxide also liberates water of hydration which can inhibit the reaction between Br and Al but its overall effect is smaller than that of the trihydrate due to its lower water content.

Even though alumina seems to have a chemical mechanism of action, its efficiency in the absence of bromine is relatively low so that fairly high concentrations must normally be used as compared with those of other flame retardants. This limits its use to polymers where considerable proportions of other materials can be incorporated without causing an unacceptable alteration in the physical or mechanical properties. Its abrasiveness may also be a disadvantage during the processing of the polymer. In conjunction with bromine, addition of 10 phr of anhydrous alumina can, however, cause a significant improvement as compared with the effect observed in the absence of the metal oxide.¹⁵²

Finally, aluminium oxides have also been found to be possible partial replacements for antimony oxide in the system Sb_2O_3 -Br-ABS.¹⁵³ At equal loadings the cost is significantly reduced and the LOI is, under certain conditions, even slightly improved. The monohydrate appears to be the most effective of the three oxides.

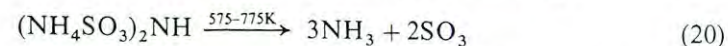
10. OTHER ELEMENTS

Various other elements may also prove beneficial in inhibiting polymer combustion, apart from the six already mentioned. They are however either less widely used or employed only for specific polymers, or relatively little understood as regards their mechanism of action.

Nitrogen is an element whose presence in a polymer appears to confer some degree of flame retardance, as shown by the rather low flammability of polyamides, both natural and synthetic. This may however be partly due to the ease of melting of these polymers so that the heat of combustion tends to be carried away from the flame. Many nitrogen-containing compounds are also used as reactive flame retardants, e.g. triazines, urea derivatives or

cyanuric acid derivatives, and it has been suggested that their action may be simply the eventual release of nitrogen which dilutes the gaseous products.¹¹ The action of ammonium salts and of nitrogen-phosphorus systems has already been mentioned.

Ammonium sulphates and ammonium sulphamates are also ammonia-releasing flame retardants by reactions 19 and 20. Their mechanism of



action is probably very similar to that of phosphates or borates, when used in conjunction with hydroxylated polymers like cellulose, since sulphate esters are formed in the condensed phase. Some other organic complexes have also been used for the sulphonation of cellulose, although this involves partial destruction of the polymer structure.¹⁵⁴ The effect of other inorganic sulphur-containing salts, including alum, with historical connotations, is probably not due to the sulphur but rather to the evolved gases. Many other inorganic salts have also been used such as, for example, carbonates or chromates. Those which do not yield gaseous products (NH_3 , H_2O , CO_2) are probably only inert fillers which dilute the solid combustible polymer and act as heat sinks. Some of them may act as catalysts for oxidative decomposition of the polymer, e.g. causing increased charring of cellulose.

Molybdenum compounds, such as molybdenum oxide or ammonium molybdate, are said to exhibit flame-retardant synergism with halogens,^{155,156} as well as being very effective smoke suppressants. In the case of MoO_3 , the metal has been found virtually quantitatively in the char, rather than in the gas phase.¹⁵⁷ The effect of molybdenum oxide on the combustion and pyrolysis of PVC is particularly interesting. Molybdenum oxide decreases the temperature for the start of the dehydrochlorination of the substrate by an ionic mechanism.¹⁵⁸ After dehydrochlorination, the additive acts as a Lewis acid to promote the isomerisation of the *cis* double bonds (formed from isotactic PVC) to *trans* double bonds.¹⁵⁹⁻¹⁶¹ In this way, the formation of aromatic products, which occurs by an intramolecular mechanism,³⁹ is inhibited. No flammable volatile products are thus formed if the heat supplied to the polymer is low, so that the molybdenum compound acts as a flame retardant. This effect does not, however, occur at the higher temperatures involved in real fires, because other volatile flammable products are then formed, mainly aliphatic straight-chain hydrocarbons; the action of the molybdenum is then

reduced to that of a smoke suppressant.¹⁶¹ Molybdenum compounds are useful as partial replacements for antimony oxide in the presence of bromine, both for polyesters¹⁶² and for ABS,¹⁵³ although there is probably no synergism between Sb and Mo. In the case of cotton fabrics, it has been found that for sodium molybdate the limiting oxygen index and the limiting nitrous oxide index show the same slope when plotted against molybdenum content, while for ammonium molybdate the slopes are different (Fig. 14).⁷² Over 90% of the molybdenum added to PVC is recovered from the char remaining after the polymer has burnt.¹⁵⁶ These findings suggest that the flame-retardant action takes place in the condensed phase but that there is some additional gas-phase effect of ammonia, particularly in nitrous oxide atmospheres. This is, of course, consistent with the other, earlier, results presented for PVC.

Hydrated tin(IV) oxide has been proposed as a good substitute for

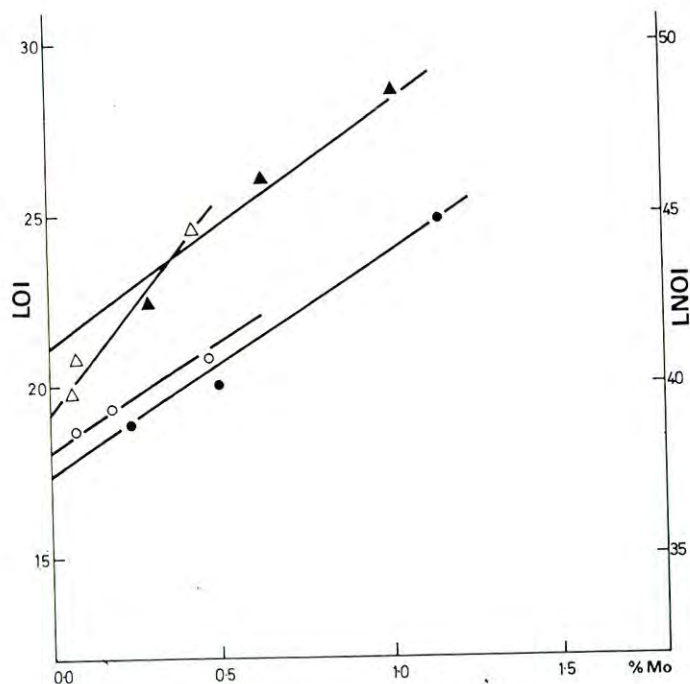


FIG. 14. Effect of molybdenum on the flammability of cotton fabrics: ○ ammonium molybdate (oxidant, O₂); ● sodium molybdate (oxidant, O₂); △ ammonium molybdate (oxidant, N₂O); ▲ sodium molybdate (oxidant, N₂O). (Reproduced from ref. 72, by courtesy of Marcel Dekker, Inc.)

antimony oxide.¹⁶³ It is possible that its effect is caused simply by the release of the water of hydration. The tin chloride is only partially volatilised³⁴ and, when used as a partial substitute for Sb₂O₃, is much less effective in increasing the LOI of ABS or of HDPE. Tin has also been used as a flame retardant for wool, particularly in the form of hexafluorostannates.^{124,163,164} In this connection it is of interest to examine the effects of titanium and zirconium, which are also widely used for inhibiting the combustion of wool as the corresponding hexafluorometallate salts.^{91,165-167} Titanium, zirconium, tin and chromium compounds exert their effects mainly in the condensed phase, as the results are largely independent of the oxidising atmosphere.^{124,168} It is probable however that it is not the metal oxide itself but a complex of the metal oxide which has adsorbed oxygen which provides the catalytic species. This would explain why nitrous oxide has a greater effect on the titanium system than on the zirconium system, both metals being very similar in all respects.¹²⁴

Ferrocene is a good smoke suppressant for thermoplastic polymers such as poly(vinyl alcohol)¹⁶⁹ or ABS,¹⁷⁰ where the gas-phase mechanism involves the total volatilisation of the iron. If butadiene is replaced by chloroprene in ABS to yield the chlorinated elastomer, volatilisation of the metal is still virtually total but the smoke-suppressant efficiency decreases considerably.¹⁷⁰ In PVC, however, the mechanism is a condensed-phase Lewis-acid type catalysis of dehydrochlorination,¹⁶⁹ analogous to that for the system PVC-MoO₃.

This review is necessarily not comprehensive since it is almost impossible to cover all the compositions that have been claimed to be effective as flame retardants in the numerous natural and synthetic polymers. An attempt has been made to deal with only those systems where the results are relatively well documented and directly amenable to interpretation.

11. CONCLUSIONS

Many different mechanisms of action have been proposed for flame retardants but these can be reduced, in principle, to a few important types, at least for the active elements most widely used in this context.

All additives which decompose thermally to yield inert gases (water, ammonia, carbon dioxide, nitrogen) will affect the flame reactions as a result of the physical dilution of the gaseous fuel and of the consequent reduction in gas temperature. Thus, of course, less heat is fed back to the condensed polymer phase. Hydrated metal oxides or salts, ammonium salts, phosphates, borates, sulphates or carbonates can act in this way.

Some additives may also function by a chemical mechanism in the gas phase; highly reactive free radicals responsible for flame propagation being replaced by less reactive species. The prime example of this behaviour consists of brominated additives, which yield gaseous hydrogen bromide. Chlorine-containing additives, although much less effective, may also act by this mechanism. Antimony trioxide, which feeds antimony monoxide into the flame zone, similarly acts by heterogeneous 'scavenging' of radicals, although it generally requires the presence of halogens to facilitate its volatilisation.

Phosphorus compounds, when added to polymers not susceptible to acid catalysis, are flame inhibitors acting partly by chemical mechanisms and possibly partly by 'blanketing' the flame to exclude oxygen. In the presence of halogens, however, the mechanism, although it may also include a 'blanketing' effect, involves mainly condensed-phase reactions.

When the substrates are hydroxylated polymers (e.g. cellulose), the mechanism of action of phosphorus-, boron- or sulphur-containing additives is an acid-catalysed esterification, which alters the condensed-phase mechanism of decomposition by enhancing char formation at the expense of volatile products. The presence of nitrogen bases, which can form P—N bonds, improves the efficiency of phosphorus esters.

Chlorine and, to a much smaller extent, bromine alter the rate of thermal decomposition of the polymer, as does the antimony oxide-halogen system, before the gas-phase inhibitors (respectively HCl, HBr and SbO—HX) are liberated. Alumina also affects the condensed-phase decomposition reactions, particularly in the presence of bromine, an effect inhibited by water. Condensed-phase effects are also found with red phosphorus, molybdates and some other metals (e.g. titanium or zirconium).

Boron can also act by two additional mechanisms: a free-radical inhibition at the gas-solid interface and the formation at the surface of the polymer of inorganic B—O deposits which insulate the substrate from the heat source.

All the mechanisms described in the section are necessarily oversimplifications, although in practice these are the modes of action used to describe the flame-retardant compounds concerned. The outline presented in Section 2 has shown polymer combustion to be a complex process involving various concurrent and consecutive stages. It is therefore to be expected that an unusual selection of properties would be required for any combination of compounds to constitute a good flame retardant. It is thus very difficult, in the present state of our knowledge, to predict successfully

what future developments are likely to be involved in the formulation of new efficient flame retardant systems.

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